

Attosecond streaking of core lines of copper dihalides

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In the attosecond (as) streaking of Cu 3s core-level photoemission of copper dihalides, we predict theoretically that the satellite ($3d^9$) is emitted later than the main line ($3d^{10}L^{-1}$; L : ligand). The emission time delay is originated from the electron correlation between the core level and 3d shell, which leads to the difference in core-hole screening between satellite and main lines. Further, we find that the time delay corresponds to a quantification of the extrinsic loss of photoemission.

During the past decade, advances in attosecond (as) ($1 \text{ as} = 10^{-18} \text{ s}$) laser technology have allowed time-resolved tracking at a time scale of the order of $\mathcal{O}(10) - \mathcal{O}(100)$ as of the photoinduced electron dynamics occurring in atoms or molecules[1–4]. A new perspective has been recently opened up by attosecond streaking metrology with the photoemission from the condensed phase[5]. Photoemission spectroscopy is one of the most developed tools for investigating the electronic structure of condensed matter[6]. The combination of attosecond metrology and photoemission spectroscopy enables time-domain insight into the electron photocreation and transport stages of the photoemission process.

In attosecond streaking photoemission, an electron emitted by an attosecond extreme ultraviolet (XUV) pulse is streaked by the femtosecond infrared (IR) pulse of a variable relative delay. The first proof of the principle experiment has revealed a time delay of about 100 as (100 ± 70 as) between photoelectrons from the localized $4f$ core level and the conduction band of a tungsten surface[5]. A large part of the observed time delay is found to be from the transport delay due to a difference in group velocities of electrons emitted from the core level and conduction band[5, 7, 8]. In a subsequent attosecond photoemission experiment for the atomic target, a different kind of time delay was observed. The slower $2s$ electrons are found to be emitted earlier than the faster $2p$ electrons by 21 ± 5 in neon atoms[9]. This time delay is not explained by the transport, but is related to the emission timing[9, 10]. The energy derivative of the quantum phase of the dipole matrix element determines this emission time delay, called the Wigner-Smith delay[11, 12]. The Wigner-Smith delay observed in neon atoms could provide a new insight into intra-atomic electron correlation, because it eventually determines the quantum phase. This naturally tempts a challenge toward a new time-domain understanding of electron correlation in a true solid with strongly correlated electrons.

Copper dihalides are insulating solids of $3d$ transition metal compounds, the simplest and best understood systems where the charge transfer scenario is applied[13]. Figure 1(a) shows that photoexcitation of the Cu core level results in two final states. The $3d^9$ final state leaves the valence configuration largely unaltered and leads to a satellite (excited one), whereas the $3d^{10}L^{-1}$ final state (L : ligand shell) transfers an electron from a ligand to

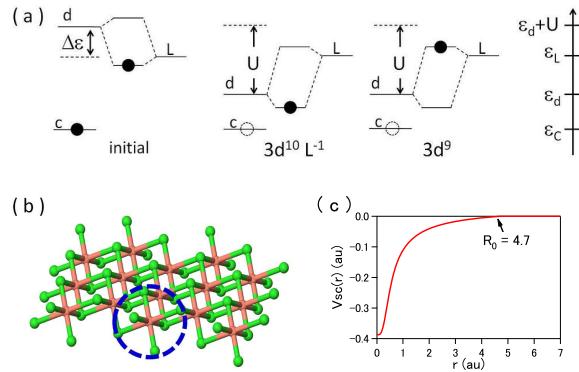


FIG. 1: (a) Copper dihalides before and after photoemission. For instance, d implies a Cu $3d$ state, c a Cu ($3s$) core level, and L a ligand, i.e., $L = (3p)^6$ of Cl for CuCl_2 . U is the electron correlation between c and d . (b) Crystal structure of CuCl_2 : a CuCl_6 cluster is designated by a blue dashed circle. (c) $V_{\text{sc}}(r)$ for CuCl_2 .

a metal ion and leads to the main line (ground one)[14]. Within this simple model, the extrinsic loss of photo-electron, that is, *loss effects due to an interaction of photoelectron with the remaining solid during its travel to the surface*, was studied in copper dihalides by Lee *et al.*[15]. Their work could provide the key inspiration to the problem of attosecond streaking photoemission of strongly correlated electron systems.

In this Letter, we study the attosecond streaking of $3s$ core lines of copper dihalides by explicitly considering the photoelectron scattering due to the core hole left after photoemission. We find that electron correlation between the core level and 3d shell leads to a difference in core-hole screening between the satellite and the main lines, which enables the theoretical prediction that the satellite is emitted later than the main line, say by 90 as (for CuBr_2), 73 as (for CuCl_2), and 40 as (for CuF_2) at $\omega_{\text{XUV}} = 141 \text{ eV}$, where ω_{XUV} is the XUV photon energy. The emission time delay strongly depends on the XUV photon energy and disappears at just $\sim 20 \text{ eV}$ over the threshold (i.e., the binding energy of the satellite). We further find that the observed time delay is a quantification of the extrinsic loss of photoemission.

Photoemission analysis of strongly correlated electron systems including d electrons could be often simplified

from their localized nature. The simplest, but quite successful model based on a molecular orbital approach, represents the d part of the system by one orbital, and the ligand by another[14]. We start from a Hamiltonian \mathcal{H}_0 of three-state (two-state + one core level) model describing copper dihalides, being consistently with Fig.1(a),

$$\mathcal{H}_0 = \varepsilon_d n_d + \varepsilon_L n_L + \varepsilon_C n_C + U n_C n_d + t(c_d^\dagger c_L + c_L^\dagger c_d), \quad (1)$$

where the first two terms depict energy levels of the Cu 3d shell ($n_d = c_d^\dagger c_d$) and a halide ligand L ($n_L = c_L^\dagger c_L$) and the last term depicts the hybridization between them. The remaining terms involve the energy level of Cu 3s core level ($n_C = c_C^\dagger c_C$) and the electron correlation U between the core level and the 3d shell. From Eq.(1), the initial ground state $|\psi_0\rangle$ is readily obtained by inserting $n_C = 1$ as $|\psi_0\rangle = -\sin\theta|C\rangle|d\rangle + \cos\theta|C\rangle|L\rangle$ with $\tan 2\theta = 2t/(\varepsilon_d + U - \varepsilon_L)$. The ground state energy E_0 is $E_0 = \varepsilon_C + \frac{1}{2}(\varepsilon_d + U + \varepsilon_L) - \frac{1}{2}\sqrt{(\varepsilon_d + U - \varepsilon_L)^2 + 4t^2}$. The final states of the target (after photoemission) are also immediately obtained by inserting $n_C = 0$ as $|\psi_m\rangle = \cos\varphi|d\rangle - \sin\varphi|L\rangle$ and $|\psi_s\rangle = \sin\varphi|d\rangle + \cos\varphi|L\rangle$ with $\tan 2\varphi = 2t/(\varepsilon_L - \varepsilon_d)$, corresponding to the main ($3d^{10}L^{-1}$) and satellite state ($3d^9$), respectively, as illustrated in Fig.1(a). The energy eigenvalues E_m and E_s are $E_m^m = \frac{1}{2}(\varepsilon_d + \varepsilon_L) \mp \frac{1}{2}\delta E$, where δE is the separation between two states given by $\delta E = \sqrt{(\varepsilon_d - \varepsilon_L)^2 + 4t^2}$. Then photocurrent is $J(\omega) = |w_m|^2\delta(\omega + E_0 - E_m) + |w_s|^2\delta(\omega + E_0 - E_s)$, where $w_m = -\sin(\varphi + \theta)$ and $w_s = \cos(\varphi + \theta)$ from $w_{m(s)} = \langle\psi_{m(s)}|c_C|\psi_0\rangle$. $J(\omega)$ can be directly compared with the left panel of Fig.2 so that the material parameters would be taken from the relative peak strengths and peak positions in the experiment[16]. This analysis constructs the sudden approximation.

\mathcal{H}_1 comprises the excitation of photoelectron by the XUV pulse and its streaking by the IR pulse,

$$\begin{aligned} \mathcal{H}_1 = & \sum_{\mathbf{k}} [\varepsilon_{\mathbf{k}} - \mathbf{k} \cdot \mathbf{A}_{\text{IR}}(\tau + \tau_{\text{IR-XUV}})] n_{\mathbf{k}} \\ & + \sum_{\mathbf{k}} m_{\mathbf{k}} (c_{\mathbf{k}}^\dagger c_C + c_C^\dagger c_{\mathbf{k}}) A_{\text{XUV}}(\tau), \end{aligned} \quad (2)$$

where $n_{\mathbf{k}} = c_{\mathbf{k}}^\dagger c_{\mathbf{k}}$ is the occupation number of photoelectron with kinetic energy of $\varepsilon_{\mathbf{k}} = \mathbf{k}^2/2$. $\mathbf{A}_{\text{IR}}(\tau)$ is the streaking IR pulse given by $\mathbf{A}_{\text{IR}}(\tau) = 0.2 \exp[-3.24 \times 10^{-5} \tau^2] \cos(0.0608\tau) \hat{\mathbf{e}}_{\text{IR}}$ and $\mathbf{A}_{\text{XUV}}(\tau)$ is the photoexciting XUV pulse given by $\mathbf{A}_{\text{XUV}}(\tau) = A_{\text{XUV}}^0 \exp[-0.036\tau^2] \cos(\omega_{\text{XUV}}\tau) \hat{\mathbf{e}}_{\text{XUV}}$. XUV and IR pulses are assumed to be linearly polarized along the direction of photoelectron detection. $\bar{\tau}_{\text{IR}}$ and $\bar{\tau}_{\text{XUV}}$ are the half width at half maximum (HWHMs) of the IR and XUV pulses, i.e., $\bar{\tau}_{\text{IR}} = 146.26$ a.u. = 3.5 fs and $\bar{\tau}_{\text{XUV}} = 4.39$ a.u. = 105 as (where a.u. means atomic unit). $\tau_{\text{IR-XUV}}$ is the relative delay of the IR pulse from the XUV pulse. $m_{\mathbf{k}}$ is $\langle \mathbf{k} | \Delta | C \rangle$ of the dipole operator Δ ($= \mathbf{r} \cdot \hat{\mathbf{e}}_{\text{XUV}}$) with $|\mathbf{k}\rangle$ as the plane wave for the photoelectron, which is equivalent to the so-called strong field approximation. Noting that the \mathbf{k} -dependence of $m_{\mathbf{k}}$ is usually weak, we take $m_{\mathbf{k}}$ just as a constant.

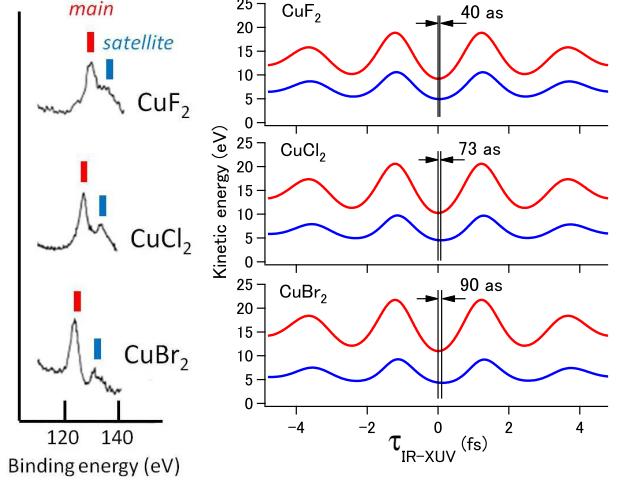


FIG. 2: Left: Photoemission spectra of Cu 3s core lines of copper dihalides[13]. Right: Centers of energy (COEs) of streaked photoemission spectra of copper dihalides with respect to a relative delay $\tau_{\text{IR-XUV}}$ of the IR pulse from the XUV pulse ($\omega_{\text{XUV}} = 141$ eV). Main lines (red lines) are prior to the satellites (blue lines).

Beyond the sudden approximation, we should consider the photoelectron scattering \mathcal{V} by the core hole as[15]

$$\begin{aligned} \mathcal{V} = & \sum_{\mathbf{kk}'} \left[n_d V_{\mathbf{kk}'}^{(d)} + n_L V_{\mathbf{kk}'}^{(L)} - V_{\mathbf{kk}'}^{(C)} \right] c_{\mathbf{k}}^\dagger c_{\mathbf{k}'} \\ \approx & n_L \sum_{\mathbf{kk}'} V_{\mathbf{kk}'}^{\text{sc}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}'}, \end{aligned} \quad (3)$$

where $V_{\mathbf{kk}'}^{(\nu)} (= \int d\mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) V^{(\nu)}(r) \psi_{\mathbf{k}'}(\mathbf{r}))$ is the matrix element of the Coulomb potential from the orbital ν using the plane wave basis. The second line is obtained by assuming that the Cu 3d level is so local as to have $V^{(C)}(r) \approx V^{(d)}(r)$ and noting $n_d + n_L = 1$. We now have $V_{\mathbf{kk}'}^{\text{sc}} = \int d\mathbf{r} \psi_{\mathbf{k}}^*(\mathbf{r}) V_{\text{sc}}(r) \psi_{\mathbf{k}'}(\mathbf{r})$ and $V_{\text{sc}}(r) = V^{(L)}(r) - V^{(d)}(r)$. $V^{(d)}(r)$ for the Cu 3d orbital, which can be calculated by generating the charge densities in terms of Slater's orbitals[17], while $V^{(L)}(r)$ would be approximated by a spherical charged shell made of six ligand orbitals of a CuCl₆ cluster (for CuCl₂) with the radius R_0 as in Fig.1(b). R_0 is an average distance between Cu and Cl. In the lowest approximation, there would be no scattering outside the cluster before reaching the surface unlike the metallic case[18]. This gives $V_{\text{sc}}(r) = \frac{1}{\epsilon} \left[-V^{(d)}(r) + \frac{1}{R_0} \right] \Theta(R_0 - r)$, where $\Theta(R_0 - r)$ is the Heaviside step function[16]. $V_{\text{sc}}(r)$ for CuCl₂ is displayed in Fig.1(c).

Under the total Hamiltonian of $\mathcal{H}_0 + \mathcal{H}_1 + \mathcal{V}$, by solving the time-dependent Schrödinger equation with $A_{\text{XUV}}^0 \rightarrow 0$, we can treat the streaking of photoemission in an exact fashion. The total wave function $|\Psi(\tau)\rangle$ at time τ can be written as

$$|\Psi(\tau)\rangle = C_d(\tau)|d\rangle|C\rangle + C_L(\tau)|L\rangle|C\rangle$$

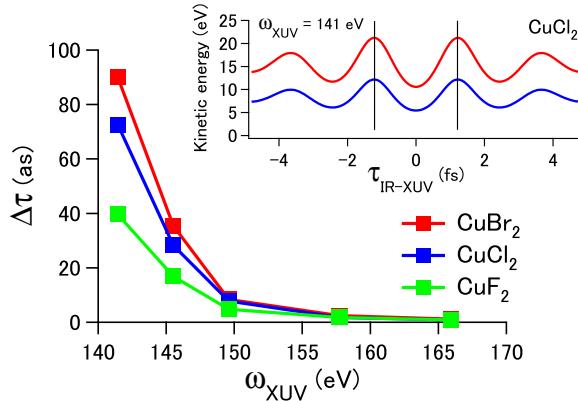


FIG. 3: Emission time delays $\Delta\tau$ between satellite and main lines for CuBr_2 , CuCl_2 , and CuF_2 with respect to ω_{XUV} . In the inset, COEs of streaked photoemission spectra within the sudden approximation, i.e., $\mathcal{V} = 0$, are given at $\omega_{\text{XUV}} = 141$ eV for CuCl_2 .

$$+ \sum_{\mathbf{k}} C_{d\mathbf{k}} |d\rangle |\mathbf{k}\rangle + \sum_{\mathbf{k}} C_{L\mathbf{k}} |L\rangle |\mathbf{k}\rangle. \quad (4)$$

Dynamics will start by turning on the XUV pulse so that the initial state should be $|\Psi(\tau_0)\rangle = |\psi_0\rangle$ given at $\tau = \tau_0 \ll -\bar{\tau}_{\text{XUV}}$. The streaked photoemission spectrogram could be calculated for the main and satellite lines as follows: $S_m(\mathbf{k}, \tau_{\text{IR-XUV}}) = |\langle \mathbf{k} | \langle \psi_m | \Psi(\tau_{\text{max}}) \rangle|^2$ and $S_s(\mathbf{k}, \tau_{\text{IR-XUV}}) = |\langle \mathbf{k} | \langle \psi_s | \Psi(\tau_{\text{max}}) \rangle|^2$ for a given value of $\tau_{\text{IR-XUV}}$. Spectrograms are found to converge at $\tau = \tau_{\text{max}} \gg \bar{\tau}_{\text{XUV}}$. In the actual calculation, we adopt $\tau_0 = -15$ a.u. and $\tau_{\text{max}} = 100$ a.u..

In the streaked spectrogram $S_m(\mathbf{k}, \tau_{\text{IR-XUV}})$ and $S_s(\mathbf{k}, \tau_{\text{IR-XUV}})$ with distributions of photoelectron kinetic energy, we determine the center of energy (COE). COEs of streaked photoemission spectra are presented with respect to $\tau_{\text{IR-XUV}}$ at $\omega_{\text{XUV}} = 141$ eV in the right panel of Fig.2. The metrology of streaked spectra reveals a time delay $\Delta\tau$ in the emission of electrons corresponding to the satellite with respect to those corresponding to the main line. This finding is dramatic. Main and satellite lines are not simultaneously created, but satellites are emitted later than main lines by $\Delta\tau = 40$ as, 73 as, and 90 as at $\omega_{\text{XUV}} = 141$ eV for CuF_2 , CuCl_2 , and CuBr_2 , respectively.

The emission time delay $\Delta\tau$ strongly depends on the XUV pulse energy ω_{XUV} as shown in Fig.3. Notably, $\Delta\tau$ already disappears at $\omega_{\text{XUV}} - E_s^B \gtrsim 20$ eV, where E_s^B is the binding energy of the satellite, $E_s^B = E_s - E_0 \approx 131$ eV, which is almost the same for the three compounds, as shown in the left panel of Fig.2. The same scattering potential \mathcal{V} also gives rise to extrinsic loss of photoelectron in photoemission spectroscopy. Extrinsic loss would give a change in relative peak strengths or an asymmetric broadening of peaks observed in the spectroscopy. It was argued that extrinsic loss due to extended excitations in a metal sustains up to the photon energy

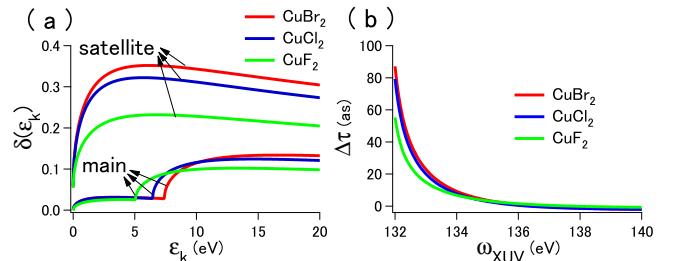


FIG. 4: (a) Energy-dependent phases of dipole matrix elements corresponding to the satellite and main lines of CuBr_2 , CuCl_2 , and CuF_2 . (b) Emission time delays $\Delta\tau$ between satellite and main lines. Photoelectron scattering is taken into account within the first-order perturbation theory.

$\sim \mathcal{O}(1)$ keV[19], whereas that due to local excitations in an electron-correlated insulator disappears at around 10 – 20 eV above the threshold[15]. In the inset of Fig.3, COEs of streaked photoemission spectra within the sudden approximation, i.e., putting $\mathcal{V} = 0$, at $\omega_{\text{XUV}} = 141$ eV for CuCl_2 are given, so that $\Delta\tau = 0$ is in fact confirmed. They indicate that $\Delta\tau$ could be a quantification of extrinsic loss contribution to the photoemission spectra of a given system.

More figurative understanding of $\Delta\tau$ is possible by noting that the Wigner-Smith delay is determined by the energy derivative of the quantum phase of the matrix element. The exact final state $|\Psi_{m(s)}^k\rangle$ in the scattering theory is $|\Psi_{m(s)}^k\rangle = \left[1 + \frac{1}{E - \mathcal{H}_0 - \mathcal{T} - \mathcal{V} - i0^+} \mathcal{V} \right] |\psi_{m(s)}\rangle |\mathbf{k}\rangle$, where E is the energy of the final state, given by $E = \varepsilon_{\mathbf{k}} + E_{m(s)}$ for the main and satellite, respectively, and $\mathcal{T} = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}}$. To the first order in \mathcal{V} , we neglect \mathcal{V} in the denominator. We can then obtain the matrix element $M_{m(s)}(\mathbf{k}) = \langle \Psi_{m(s)}^k | \Delta | \psi_0 \rangle$. The quantum phase of the matrix element will be $\delta_{m(s)}(\varepsilon_{\mathbf{k}}) = \arg[M_{m(s)}(\mathbf{k})]$, the behavior of which is given in Fig.4(a). The time delay $\Delta\tau$ between the satellite and main lines is calculated by $\Delta\tau = \partial\delta_s(\varepsilon_{\mathbf{k}})/\partial\varepsilon_{\mathbf{k}} - \partial\delta_m(\varepsilon_{\mathbf{k}})/\partial\varepsilon_{\mathbf{k}}|_{\varepsilon_{\mathbf{k}} + \delta E}$ and given with respect to ω_{XUV} in Fig.4(b), which could be compared with Fig.3. Suppression of $\Delta\tau$ with ω_{XUV} is much faster in the first-order perturbation so that $\Delta\tau$ disappears at $\omega_{\text{XUV}} - E_s^B \gtrsim 5$ eV. Perturbation theory cannot give quantitatively good results compared to the exact ones in Figs.2 and 3 due to the strong scattering potential, but could give intuitive understanding that the Wigner-Smith delay occurs mostly in satellite, especially in the low energy region, i.e., $\partial\delta_s(\varepsilon_{\mathbf{k}})/\partial\varepsilon_{\mathbf{k}} \gg \partial\delta_m(\varepsilon_{\mathbf{k}})/\partial\varepsilon_{\mathbf{k}}|_{\varepsilon_{\mathbf{k}} + \delta E}$.

A strong electron correlation between the core level and the 3d shell plays an essential role in inducing the emission time delay between the main and satellite lines in copper dihalides. The electron correlation U leads to two final states with different screening of the core hole created after photoemission. The larger the U , the greater the difference. When keeping the

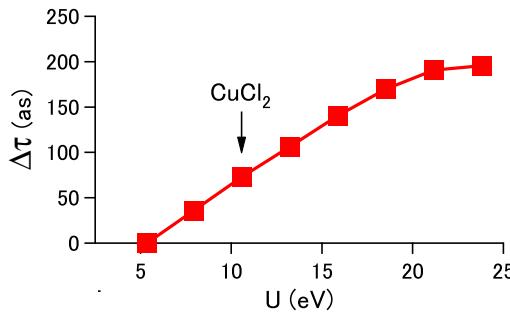


FIG. 5: Emission time delays $\Delta\tau$ with respect to U at $\omega_{\text{XUV}} = 141$ eV obtained by keeping the same initial state by fixing the value of $\varepsilon_d + U$ ($= 2.4$ eV as in CuCl_2). All other material parameters are taken from CuCl_2 .

same initial state by fixing the value of $\varepsilon_d + U$, as illustrated in Fig.1(a), we may have $|\psi_m\rangle \rightarrow |d\rangle$ and $|\psi_s\rangle \rightarrow |L\rangle$ in a limit of large $U \rightarrow \infty$, and $|\mathbf{k}\rangle|\psi_m\rangle$ will not be scattered by the scattering potential \mathcal{V} , i.e., *perfect screening*, while $|\mathbf{k}\rangle|\psi_s\rangle$ is maximally scattered, i.e., *no screening*. This will cause an increase of $\Delta\tau$, which is clearly demonstrated in Fig.5. It should also be noted that the correlation U scales the potential strength, i.e., $U = -V_{\text{sc}}(0)$ [16]. From $\Delta\varepsilon \approx U$ under an assumption of small hybridization (See Fig.1(a)), main and satellite lines would overlap at $U \approx 5.3$ eV and $\Delta\tau$ would then vanish.

Finally, we note that the transport delay occurring inside the solid was not considered here. However, such transport delay could be separated from the Wigner-Smith delay because it stems simply from different group velocities between satellite and main lines without additional scattering[18]. Further, if an atom-thick adsorbate is technically possible with copper dihalides, the transport delay may in principle be removed in the experiment.

To summarize, we explored the attosecond streaking of $3s$ core lines of copper dihalides by incorporating a model of copper dihalide cluster to describe the photoelectron scattering. We found that in the emission timing, the satellite comes later than the main line. Such an emission time delay originates from the electron correlation between the core level and the $3d$ shell, which leads to different core-hole screening depending on satellite and main lines. The time delay strongly depends on ω_{XUV} and its disappearance is energetically rapid, i.e., at just ~ 20 eV above the threshold. To our best knowledge, this is the first study to explore the emission timing of electrons in a true solid with strong electron correlation. Lastly, we claim that the time delay has the same root in the extrinsic loss of photoelectrons and it is a quantification of extrinsic loss.

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[16] The necessary parameters for copper dihalides are well tabulated in Ref.[15]: $U = 8.62$ eV, $t = 1.63$ eV, $\delta E = 5.41$ eV, $\varepsilon_L = -4.3$ eV, and $R_0 = 3.86$ a.u. for CuF_2 , $U = 10.58$ eV, $t = 1.84$ eV, $\delta E = 6.45$ eV, $\varepsilon_L = -2.9$ eV, and $R_0 = 4.71$ a.u. for CuCl_2 , $U = 12.33$ eV, $t = 2.02$ eV, $\delta E = 7.37$ eV, $\varepsilon_L = -1.96$ eV, and $R_0 = 5.01$ a.u. for CuBr_2 , respectively. The value $\varepsilon_C = -130.6$ eV is taken as common to three compounds. Finally, ϵ is a constant to match $V_{\text{sc}}(0) = -U$: $\epsilon = 2.26$, 1.96 , and 1.71 are found for CuF_2 , CuCl_2 , and CuBr_2 , respectively.
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